CHAPTER 2. REVIEW OF THIN FILM SILICON NITRIDE

2.1 Introduction

Glow discharge silicon nitride thin film is normally crystallographically amorphous. Unlike CVD silicon nitride thin film deposited at high temperature, glow discharge film grown at lower temperature is not confined to the stoichiometric Si_3N_4 composition. It contains much larger amount of hydrogen, typically 15 at% to 40 at%. Frequently oxygen is also incorporated. Thus its compositional description is actually $SiN_xH_yO_z$ [1].

Silicon nitrides are important materials currently used in isolation technology to manufacture Very Large Scale Integrated circuits (VLSI) [2]. High temperature Chemical Vapour Deposited (CVD) nitrides are applied in the local oxidation processing sequence as oxidation barrier and also in Metal-Nitride-Oxide (MNO) semiconductor memory structures, or Oxide-Nitride-Oxide (ONO) structures [3]. Low temperature deposited versions of these materials are applied as intermetal layers, passivation layers, or in ONO structures where the processing temperature is limited [4]. Silicon Nitride compound has excellent diffusion-limiting properties and hence acts as a barrier against impurity diffusion and contamination by preventing sodium diffussion and moisture penetration [2]. Furthermore silicon nitride oxidizes very slow and prevents the underlying silicon from oxidizing itself. This process of selective oxidation produces nearly planar device structures [2]. It also protects Al and Au interconnection circuits from scratches and damages because of its hardness and good scratch resistance [5,6,7]. Other properties which make silicon nitride attractive for the semiconductor processing applications are its good adhesion to

silicon, III-V compound semiconductors, other dielectrics and most metallization including Au, and also its rapid and uniform plasma etching characteristics [1]. Silicon Nitride applications are also found in solar-cell technology as anti-reflection coatings and tunnel dielectrics [8].

The following section shall review the various techniques that are utilized to fabricate the silicon nitride layers. More emphasis is given on glow discharge method as this technique is related to the present work. Detail discussions on the glow discharge method shall focus on the reaction mechanism, the system configuration, and consequently the material properties obtained from the above mentioned method.

2.2 Preparation Technique for Silicon Nitride

A large number of techniques have been applied in the fabrication of silicon nitride layers. In current Si based integrated technology, methods like CVD at low gas pressure (also known as LPCVD) and high temperature (700-900°C), and Glow Discharge Deposition (also commonly known as Plasma-Enhanced Chemical Vapour Deposition, PECVD) at relatively low temperature (below 400°C) are used. In principle these methods allow thick films to be grown with no direct fundamental limitation on the final film thickness. Nevertheless, in both cases of preparation the resulting materials are by no means unambiguously defined. In thermally activated CVD processes, different temperature, gas-phase composition, total pressure and even different order of introducing the reactant gaseous into the reactor resulted in materials with different properties. As regards to the glow discharge process, one can add to the above mentioned factors the variation of frequency and rf power with which the plasma is excited, and in some circumstances whether or not the growth

surface is in direct contact with the plasma [9]. More over the inference that these reactor parameters interact with others makes the situation even more complex [10]. Other methods of silicon nitride preparation include reactive ion-beam sputtering and nitrogen implantation in silicon.

2.21 Chemical Vapour Deposition

CVD is a purely chemical process that produces solid products by the thermal reaction from several gases at high temperature [11]. Silicon nitride can be deposited by reacting silane and ammonia gases at atmospheric pressure and of temperatures between 700-900°C, or by reacting dichlorosilane and ammonia at reduced pressure and at temperatures between 700-800°C [2]. The chemical reactions are represented by

$$3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$$

$$3SiCl_2H_2 + 4NH_3 \rightarrow Si_3N_4 + 6HCl + 6H_2$$

These high temperature CVD nitrides may contain a few at.% of bonded hydrogen in the N-H and Si-H bonding configuration [12], with the N-H groups outnumbering the Si-H groups and the hydrogen concentration decreases with increasing temperature.

2.22 Glow Discharge Deposition

Glow discharge deposition is essentially the extension and enhancement of the previous technique by using a plasma [11]. It is sometimes referred to as Plasma-enhanced CVD (PECVD), plasma-assisted CVD (PACVD), reactive plasma deposition (RPD) or plasma deposition (PD). However the term glow discharge shall be adopted throughout the present work. As in CVD, all the chemical constituents of

the deposited films are introduced in the gaseous phase where the reactions occur within a low temperature plasma glow discharge. The electric field ionize the gases which tend to create active species that react at the substrate's surface. Therefore film formation process in glow discharge involves not only chemical reactions but additionally involves physical processes such as ion and electron bombardment of the growing film. Thus the plasma condition makes it possible for the reaction temperature to be lower than in that thermal CVD. Silicon nitride is formed by reacting silane either with ammonia or nitrogen discharge. The reactions are often assumed to be [2]

$$SiH_4 + NH_3 \rightarrow SiNH + 3H_2$$

$$2SiH_4 + N_2 \rightarrow 2SiNH + 3H_2$$

The major attraction of glow discharge is its useful deposition rate at a temperature significantly lower than that for CVD, that is in the range 200-350°C compared to typical CVD temperatures of 400-900°C [1]. As a result, it is possible to grow films on substrates that might not have the thermal stability to accept such coatings, for instance the high temperature required for thermochemical reactions between source gases to obtain stoichiometric Si_3N_4 has limited applications since Al and Au are used in interconnections of semiconductor devices. By applying glow discharge technique it is now possible to deposit Si-N film at a temperature lower than the melting points of Al and Au, and even at substrate temperature as low as several tens of degrees Celcius. Nevertheless glow discharge has other disadvantages such as the incorporation of pinholes arising from plasma bombardment and hydrogen incorporation into the films (5-30 at%) [13,14]. H incorporation is caused by the nitride's low preparation temperature and hence the decomposition of the

hydrogen-containing molecule gas is not complete and large concentrations of hydrogen are incorporated. Frequently small amount of oxygen are also incorporated into the film, particularly close to the substrate interface, dettered in the initial stages of deposition [1].Therefore glow discharge silicon nitride films are not one material confined to the stoichiometric Si_3N_4, but a whole family of materials. However for the sake of simplicity, the film usually expressed as $Si_xN_yH_z$ as shown in the above equation or just in the abbreviated form SiN_x [1]. The composition x, y and z depends on the deposition parameters.

Among the early literatures concerning plasma-deposited silicon nitride were reports by Sterling and Swan [15], Sinha et al and Lanford et al [16,17]. A number of different plasma reactors were commercially available in the early 1980s [18]. The plasma tecnique currently used in all commercial reactors is a low pressure glow discharge developed in a radio frequency (r.f.) field [13].

2.23 Reactive Ion-Beam Sputtering

Low temperature (virtually) H-free silicon nitride films can be prepared by reactive ion-beam sputtering [19,20]. In this technique, a silicon target is sputtered in a nitrogen-bearing gas which may or may not be diluted by an inert carrier gas such as argon. In the simplest case, sputtering is carried out in pure N_2. Reactive ion-beam sputtering methods have been shown to afford the possibility of obtaining a wide range of film composition [21]. Stoichiometric silicon nitride layers are obtained at low ion-beam energy that is below 400 eV, but at a very low growth rate [19,22,23]. Si_3N_4 stoichiometry and N-rich film can be obtained by introducing some NH_3 in the deposition chamber [19,23]. However this can results in H-incorporation coming

from the Si-H and N-H groups [23]. The room temperature H-free ion-beam sputtered nitride films, both of stoichiometric and Si-rich, appear to exhibit a high chemical and thermal endurance, a good oxidation resistance and a low density of memory traps [20,24].

2.24 Nitrogen implantation

High-dose low-energy ion implantation has been applied to prepare superficial stoichiometric silicon nitride [25-27] films with thickness within 7-10 nm. At the same time a damaged layer in the substrate is created, detected by using Rutherford Backscattering (RBS) and cannot be restored when annealed at temperatures below 1000°C [28]. Ion implantation from high doses of oxygen or nitrogen followed by very high temperature annealing allows the formation of buried SiO_2 and Si_3N_4 layers in Si [7], thus giving rise to the so-called silicon on insulator (SOI) structures. Such technologies for obtaining SOI structures are called separation by implanted oxygen (SIMOX) and separation by implanted nitrogen (SIMNI) [7]. For this the implantation dose has to be larger than a threshold value, which is defined as the dose for which the stoichiometric concentration of the compound is achieved at the implantation peak. The threshold dose of nitrogen atomic implantation is estimated to be about 7.6×10^{17} cm^{-2} for an implantation energy of 75 keV, as calculated by TRIM simulation [7]. These SOI subtrates have been successfully used for etch-stop applications as both materials exhibit a strong resistance to the usual Si etchants, the structures being very stable under further thermal treatments. Nitrogen has several advantages in relation to oxygen for these applications since silicon nitride is known to be more efficient as an etch-stop material compared to silicon oxide.

Moreover, and opposite to oxygen, the implantation of nitrogen needs no special implantation system since it is possible to obtain relatively high currents with conventional machines. However the SOI substrates are quite expensive as they involve the use of high dose dedicated ion implanter machines and very high temperature annealings [7]

2.3 Reaction Mechanism in Glow Discharge Deposition

A plasma is by definition, a collection of particles consisting electrons, ions and excited molecules or atoms in which there are equal numbers per unit volume of electrons and ions (charge neutrality). It is characterised by the electron energy,kT_e and electron density,n_e. Plasmas which are used for preparation of thin films are mainly those generated under the category of glow discharge within the pressure range of 0.1-10 Torr, where typically $n_e \cong 10^{10}$ cm^{-3} and kT_e is approximately 1-10 eV. A typical characteristic of this plasma is its lack of thermal equilibrium between the electron temperature and gas temperature as the degree of ionization is less than 10^{-5}. Plasma in the state of thermal non-equilibrium is called Cold Plasma and the electron temperature can be as high as 20000-30000 K, while the heavy particles and the reactant chamber on the other hand will remain at room temperature [11].

The reaction mechanisms involved in glow discharge film formation are not quite well understood due to the complexity of the reaction within the cold plasma, i.e. the cold plasma is not in thermal equilibrium, the gases used are usually polyatomic molecules and the lack of basic data such as reaction cross sections. Furthermore gas phase reactions in the plasma and the surface on the substrate contribute roughly equally to the thin film formation.

A qualitative description of the film formation mechanisms might identify three major stages, namely radical and ion generation in the plasma, radical adsorption and ion incorporation on the film surface, and finally surface adatom (adsorbed or attached atom) rearrangment [29].

Radicals and ions are generated from inelastic collisions between electrons and gas molecules. Ionization is as a result from collisions at higher energies, while collisions at lower energies produce excited molecules and radicals. This is due to the fact that the energies of the electrons in the discharge have a non-Maxwellian distribution with unsymmetrical tails [30]. Table 2.1 summarizes the possible inelastic collisions that can occur in the glow discharge.

These plasma species diffuse to the substrate surface, migrate and seek for adsorption sites on the substrate. The radicals have higher sticking coefficients compared to the ionic species and therefore the radicals can be easily adsorbed onto the substrate surface, while being subjected to a variety of interactions including electron and ion bombardments, rearrangements, reactions with other adsorbed species, new bond formation and finallly film formation and growth. Surface reaction is affected by bombardments of radicals and ions and simultaneously dissociation and sputtering may occur due to these bombardments.

Adatom rearrangement is an important stage in the film growth, where the adsorbed atoms diffuse into stable sites on the surface. Concurrent with film growth is the requirement for desorption of reaction by-products from the film surface. Desorption rates and adatom diffusion rates are strongly influnced by the substrate temperatures whereby higher temperatures favour films with fewer entrapped by-products, higher densities and more uniform composition.

COLLISION PROCESS	SPECIES FORMED
Excitation	$e + A \rightarrow A^* + e$
Dissociation	$e + A_2 \rightarrow 2A + e$
Ionization	$e + A \rightarrow A^+ + e$
Attachment or Capture	$e + A \rightarrow A^-$
Dissociative ionization	$e + A_2 \rightarrow A^+ + A + 2e$
Dissociative attachment	$e + A_2 \rightarrow A^- + A$
Dissociative recombination	$e + A_2^+ \rightarrow 2A$
Charge transfer	$A^+ + A \rightarrow A + A^+$
Penning dissociation	$A_2^* \rightarrow 2A$
Penning ionization	$A^* + B \rightarrow A + B^+ + e$

Note: 1. A and B can be either an atom or molecule

2. A_2 is a molecule

3. e is an electron

Table 2.1. Possible inelastic collision to occur in low-pressure glow discharge plasma, after ref.[31]

Many reactions can occur among the excited molecules or atoms, among the ions and molecules and etc., which further complicates the reaction mechanisms. A schematic diagram showing the reaction of plasma species during thin film formation is given in Figure 2.1. Even though reaction mechanisms are not fully understood, numerous applications to film formation has been applied because of the technological demands from industries.

In principle, by adopting source gases which contain the desired elements, any film can be deposited by glow discharge decomposition. Table 2.2 lists a number of nitride films that has been deposited by glow discharge method. Glow discharge deposition of silicon-nitrogen compound combines a silicon-containing gas with a nitriding agent. Monosilane (SiH_4) is the common source of silane and typically used nitriding agents are ammonia (NH_3) and nitrogen (N_2). The overall equation describing the reactions to produce nitride films is [13]

$$SiH_4 + NH_3 \text{ or } N_2 \rightarrow Si_xN_yH_z + H_2 \text{ (at 200-400°C)}$$

When the latter serves as the nitrogen source, large N_2/SiH_4 ratio (10^2-10^3) are needed to produce films with stoichiometry approaching that of Si_3N_4 , as N_2 dissociation rate is much lower than that of SiH_4 [31,32]. In contrast, NH_3 can dissociate in a series of low energy steps that readily provide active nitrogen species for film formation, and hence the NH_3/SiH_4 ratios can be considerably lowered to 5-20 [31]. The use of N_2 in place of NH_3 , however, offer a few advantages that is, it is non-corrosive, non-flammable and free from water contamination [33]. Also the resulting films may contain less hydrogen. Some possible glow discharge reaction which are pertinent to Si_3N_4 formation are listed in Table 2.3 [34].

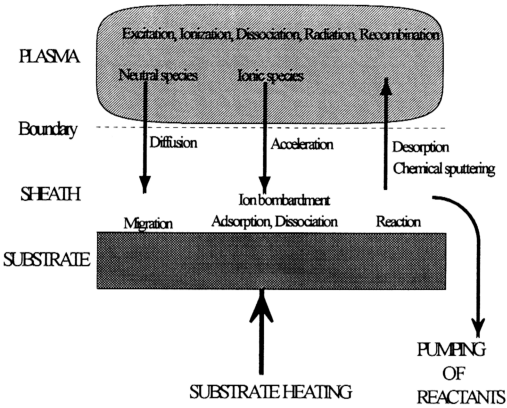

Figure 2.1. Schematic representation of the PECVD reaction processes, after ref.[11]. The sheath along the electrode surface is referred to as the physical surface where the plasma is bounded and the electrical neutrality of the plasma is no longer maintained.

FILM	DEPOSITION TEMPERATURE °C	DEPOSITION RATE Å/s	SOURCE GASES
Si-N	25-500	1-10	$SiH_4/NH_3/N_2$
			$SiH_4/NH_3/Ar$
			$SiH_4/NH_3/He$
			$SiH_4/NH_3/H_2$
			SiH_4/NH_3
			$SiH_4/N_2/Ar$
			$SiH_4/N_2/He$
			$SiH_4/N_2/H_2$
			$SiH_4/NF_3/N_2$
			SiH_4/N_2
			$SiH_4/NF_3/N_2$
			$SiF_2/N_2/H_2$
			SiH_2Cl_2/NH_3
			SiI_4/N_2
			HMCTS*/NH_3/N_2
BN	300-700	1-50	B_2H_6/NH_3
			$BCl_3/NH_3/Ar$
			$BH_3N(C_2H_5)_3/NH_3/Ar$
AlN	< 1000	100	$AlCl_3/N_2$
			$Al(CH_3)_3/H_2/NH_3/(N_2)$
P_3N_5	360-400	< 500	P/N_2
GaN	< 600	1-10	$GaCl_4/N_2$
Ti-N	250-1000	1-30	$TiCl_4/N_2/H_2$
			$TiCl_4/NH_3/H_2$
SbN	150-500	0.05-0.3	$SbCl_3/N_2/H_2$
			$SbCl_3/NH_3/H_2$

* 1,1,3,3,5,5-Hexamethylcyclotrisilazane

Table 2.2. Nitride films produced from PECVD, after ref. [11].

IONIZATION REACTION	eV	BOND STRENGTH	eV
$SiH_4 \rightarrow SiH_3^+ + H + e$	12.2	$SiH_4 \rightarrow SiH_3 + H$	4.07
$SiH_4 \rightarrow SiH_2^+ + H_2 + e$	12.2	$SiH \rightarrow Si + H$	3.09
$NH_3 \rightarrow NH_3^+ + e$	10.2	$NH_3 \rightarrow NH_2 + H$	4.76
$NH_2 \rightarrow NH_2^+ + e$	11.4	$NH_2 \rightarrow NH + H$	3.9
$NH \rightarrow NH^+ + e$	13.1	$NH \rightarrow N + H$	3.42
$N_2 \rightarrow N_2^+ + e$	15.57	$N_2 \rightarrow 2N$	9.83

Table 2.3. Ionization energies and bond strengths for some possible plasma reactions occuring in silicon nitride formation, after ref. [31].

Introducing an inert carrier gas to the reactant mixtures, such as argon and helium at low pressure can help in improving wafer-to-wafer uniformity This is due to enhanced reactant diffusion to the substrate surface and more effective electron energy transfer to the reactant gases. At lower pressure, gas diffusivity increases, thus allowing a surface controlled reaction [31]. Inert gas can absorb electron energy in the discharge and be excited into a metastable state. The metastable atoms transfer their energy to other gases via inelastic collisions (Penning effect). This process led to an increase in the ions and radicals population uniformly throughout the plasma and thereby improving deposition uniformity [31]. Table 2.4 shows metastable and ionization energy levels for some inert and diatomic gases.

2.4 Glow Discharge System Design

All plasma deposition systems consists of gas sources, gas flow controllers, a gas manifold and distributor, a plasma chamber incorporating a heated substrate table and pressure monitoring, an rf generator, a pumping system including throttle valve, and an exhaust system as shown schematically in Figure 2.2. It is the design of the plasma chamber itself, in particular the electrode and gas flow geometries which distinguishes the various types of glow discharge reactor [1].

There are many geometries and physical arrangement possible for glow discharge reactors but there are three main types that has proven to be of commercial values [35] that is the parallel-plate radial flow reactor (also referred to as Reinberg reactor), tube and barrel reactor, and the final type is the hot wall tube. Figures 2.3-2.5 show schematically these three main categories respectively, together with the relevant sub-categories. The radial flow and hot tube reactors are used for uniform

depositions of dielectric films over large batches of wafers whereas tube reactors are normally used for resist ashing or non-critical process where uniformity is not of great concern [35].

The parallel-plate radial flow reactor is the most commonly employed for plasma deposition. It was originally designed by A.R.Reinberg [1] for silicon nitride deposition. The original design, Figure 2.3a, employed inward radial flow. Unreacted gases are introduced at the periphery of the electrode and then flow inward where they are exhausted at the centre. Substrates are placed horizontally on the lower and grounded electrode. As the reactant gases flow inward across the electrode, their concentration are depleted while the by-products concentration increases. This might be expected to result in unacceptable deposition uniformity were it not for two factors. The first factor is that the electron density is typically higher toward the centre of the electrode structure due to diffusion to reactor wall [30], and another factor is that the reactant gas velocity increases as it flows a decreasing area toward the centrally located exhaust port. By making a proper choice in the conditions, the opposing effects can be balanced to optimize uniformity. Figure 2.3b shows a latter design [1] of the shower-head variety and utilizing an outward flow. This type employs a perforated upper electrode, through which the reactant gases are introduced into the plasma. An advantage of this scheme is that the lower electrode (substrate table) is a continuous plate, in contrast to the annular geometry required for radial flow.

Figure 2.4 depicts the second type of reactor, that is the tube or barrel reactor which as in the previous type, is cold wall. The rf power is usually inductively coupled by a coil around the tube which is external to the plasma region. Capacitive coupling

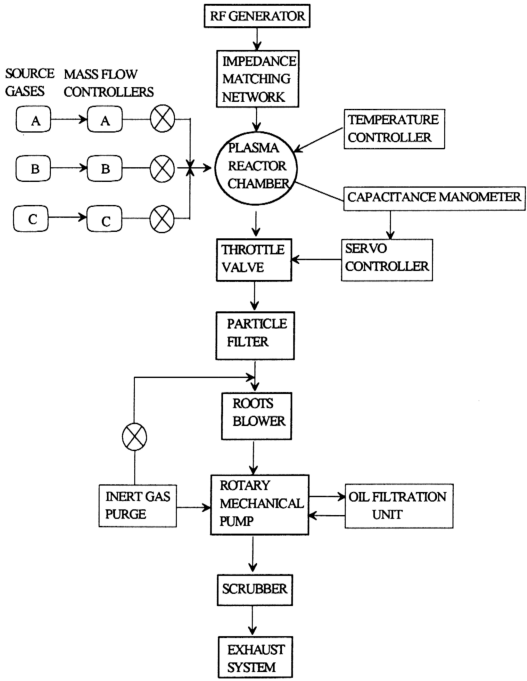

Figure 2.2. Schematic representation of the components in a typically glow discharge system, after ref. [1].

GAS	DISSOCIATION ENERGY eV	METASTABLE ENERGY eV	IONIZATION ENERGY eV
He	---	19.8	24.53
Ne	---	16.62	21.56
Ar	---	11.55	15.76
H_2	4.5	---	15.6
H	---	10.1	13.56
N_2	9.8	---	15.5
N	---	2.38	14.5

Table 2.4. Energy levels of inert and diatomic gases, after ref. [31].

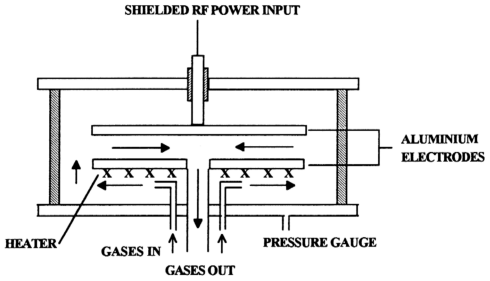

Figure 2.3(a)

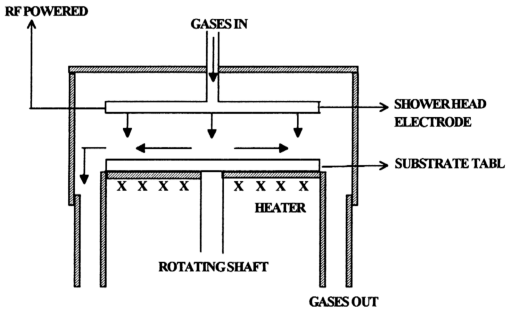

Figure 2.3(b)

Figure 2.3. The parallel-plate radial flow reactors.

(a) parallel-plate with Reinberg-design inward radial flow.

(b) modified design with outward radial flow and shower-head gas distribution.

via external electrodes is possible. This type of reactor is very simple in design and lends itself to process research studies, but however is not suitable for uniform batch deposition that is needed in a production environment. In this reactor the substrate is not directly exposed to the plasma but is mounted downstream from the glow region and hence it is particularly suitable for indirect plasma studies. As the substrate is within the field-free region, only plasma species with sufficiently long lifetime can reach the substrate and as a result the bombardments of energetic ions and radicals onto the substrate can be avoided. This is beneficial for avoiding or restricting substrate damage effect but on the other hand may not be beneficial to film preparation.

The hot wall tube is basically a diffusion furnace tube into which is inserted a multiple array of rectangular parallel-plate electrode pairs (usually made of carbon), so that it assumes a uniform high temperature (see Figure 2.5). The carbon fabricated electrodes can give rise to particulate contamination in some situation [35]. This reactor is to some extent a sub-division of Reinberg reactor in that an individual pair of electrodes forms the parallel-plate. Alternate electrodes are connected to the rf power lead while the others are grounded. Each grounded electrode can carry a single wafer in a verticle orientation. This arrangement is suitable for large, regularly shaped Si wafers where its advantage is in its large wafer capacity A commercially avaible system has a batch capacity of 84 four inch wafers. However in many applications, the process cycle time is rather longer than that of the radial flow reactors. Since the gas mixture flows down the tube and a plasma is generated, there is a pressure gradient down the tube (thus reducing residence time) and the gas composition changes because of depletion. It would appear that the only way to achive uniform

deposition is to use a large excess of reactants and hence operate at low efficiency. The result is possibly a costly operation if very high purity silane is being used. One variation of this type of reactor [1] pulses the applied rf power to prevent downstream depletion of reactants.

All the types of reactors discussed can be operated at high or low frequency but 13.56 MHz is generally used for tube reactors. Low frequency operation is simpler in that impedance matching is accomplished by a variable transformer, whereas high frequency impedance matching requires an LC network. Possibly because of the difficulty of impedance matching low frequency is usually used in the case of complex electrode arrangement in a hot-wall reactor.

An interesting recent development of a glow discharge method is the electron beam assisted chemical vapour deposition (EBCVD) [1]. In this technique, a 2.5 cm wide, shallow electron beam of a few keV energy is injected into the reactive gases parallel to and a few mm above the substrate surfaces, in much the same way as an excimer laser beam was used by the same group for laser photo assisted CVD [1]. A localized plasma is created from which excited and reactive radicals diffuse to and react on the heated substrate surface. Source gas compositions, flow rates, pressure, and substrate temperature are similar as for conventional glow discharge deposition. However, the advantage of this method is that the substrate do not sit on one of the electrodes responsible for maintaining the plasma.Since there is only small angle scattering of the injected electrons, the substrate surface is largely free of energetic electron bombardments. However, since the substrate carrying electrode is itself a

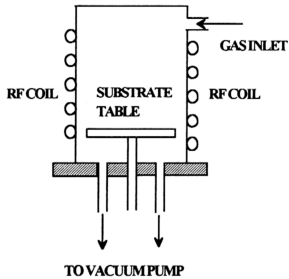

Figure 2.4(a)

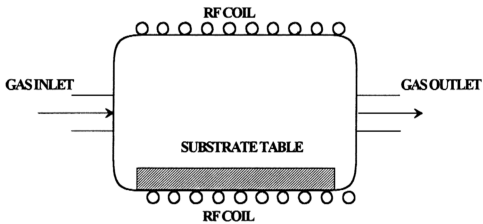

Figure 2.4(b)

Figure 2.4. Inductively coupled reactor utilizing external coils. In (a) the substrates are placed outside of the glow region, while in (b) the substrates are exposed directly to the glow discharge.

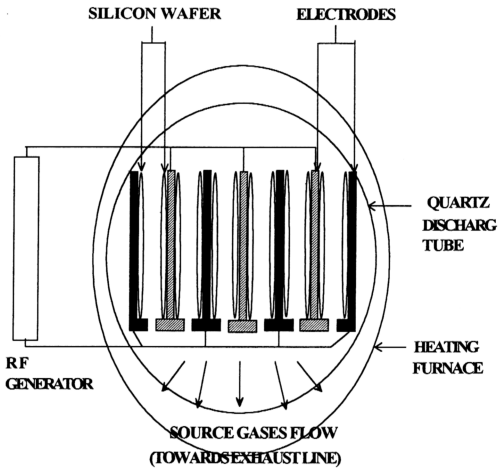

Figure 2.5. Cross-section of a longitudal flow hot wall tube reactor displaying the multiple array parallel-plate electrode pairs placed in a diffusion furnace.

boundary to the localized plasma located above it, the glow region genarally acquires a small positive bias relative to the substrate which results in a sheath regions being formed. As a consequence the substrate is subjected to low energy, positive ion bombardments. The energy distribution of this ion bombardments is expected to be similar to that originating from a conventional, high frequency rf plasma, although the ion flux may be lower. Thus the technique has some of the benefits of the indirect plasma deposition, but without the substrate being so remote from the plasma. Therefore the penalty of reduced deposition rate is avoided.

For a given reactor geometry, the gas composition, flowrate, pressure, substrate table temperature, rf frequency and power level are all varied in an attempt to achive the best results for film quality. Some variables have a predictable effect on deposition, for instance the deposition rate generally increases with increasing power or reactant pressure. On the other hand, in other cases the variables can affect the deposition and film properties but such effects are more difficult to explain. Moreover there are variables that tend to interact with one another, thus make measuring and interpreting the effect of a specific variable difficult. The strong dependance on deposition conditions makes it difficult to compare films prepared from different reactors. All deposition conditions must be carefully specified when discussing the properties of plasma-deposited materials [2].

2.5 Properties of Glow Discharge Silicon Nitride

A wide variety of measurements have been reported for glow discharge silicon nitride films resulting from a wide range of deposition conditions that are encountered

and also the interrelation of the deposition parameters, preparation techniques utilized and the basic complexity of the silicon-nitrogen-hidrogen system.

2.51 Chemical Bondings

Infrared (IR) spectroscopy yields the most direct information which can indicate the local bonding environment of the constituent atoms and hence the molecular structure in the deposited films [17,36]. A typical IR spectrum of a plasma nitride film deposited at 300°C is shown in Figure 2.6. The significant IR bands in glow discharge silicon nitrides are identified as Si-N (870 cm^{-1}) asymmetric stretching mode (s); $N-H_2$ (3445cm^{-1}), N-H (3330 cm^{-1}) and Si-H (2150 cm^{-1}) which are related to stretching modes; and N-H (1180 cm^{-1}) and $N-H_2$ (1540cm^{-1}) which are related to bending modes [13]. The main absorption band of nitride film on silicon wafer at room temperature lies between 700-1100 cm^{-1} and peaks approximately at 820 cm^{-1}. A gradual change in the absorption peak from 870 to 820 cm^{-1} was observed for a change in silane concentration from 0.1 to 2.5 mol % [37].

Hydrogen-related bonds, in the form of Si-H and N-H, are readily observable in nearly all plasma nitrides films except those that are formed at extreme temperature or power [32,38]. High temperature or high power increases the amount of bond breaking during deposition and results in films with low H contents [39,40]. The total amount of bonded hydrogen is typically in the range 18-22 at.% for deposition temperatures of 275-380°C with the silane-ammonia reaction [31] and as high as 39 at.% for deposition temperature of 150°C [18]. Experiments using deuterated reactants [41] show that 80-90% of the total H in a Si-N films deposited from SiH_4

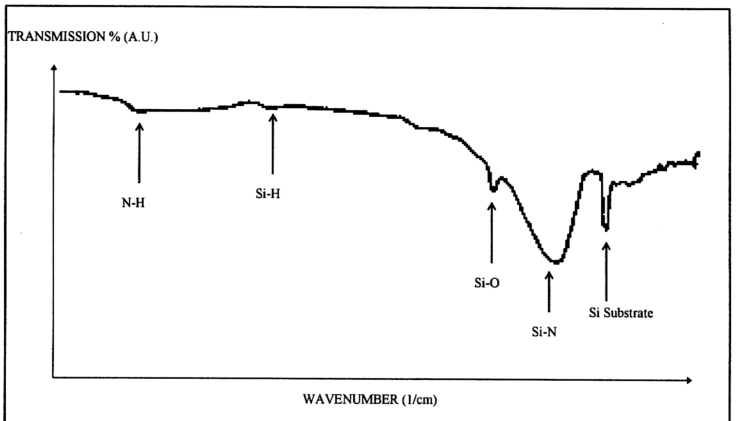

Figure 2.6. A typical FTIR transmission spectrum of Si_xN_y:H thin film in the range of 4000 cm^{-1} to 200 cm^{-1}

and NH_3 is introduced from NH_3 not from SiH_4. Thus lower hydrogen content has been observed in films deposited from nitrogen as nitriding agent [32].

An appreciable amount of oxygen in the form of Si-O bonds can also be detected in glow discharge silicon nitride films. The oxygen content was found to vary from 2 at.% for films deposited at temperatures of 250°C to 13 at.% for deposition temperatures of 100°C. Evidence of oxygen incorporation is also provided by the lower refractive index of silicon nitride films obtained at lower deposition temperatures for similar reactant gas ratios. For a NH_3/SiH_4 ratio of 10, the refractive index of a film deposited at 380°C is 2.00, while deposition at 300°C results in a refractive index of 1.95 [31]. The large amount of oxygen incorporated at low deposition temperatures is believed to be due to moisture or oxygen released from surfaces of the reaction chamber. At higher temperatures the moisture is more likely to be desorbed from the walls and pumped out prior to deposition [42]. Traces of carbon that are sometimes observed may be attributed to backstreamed oil vapour from the mechanical pumps or possibly from the SiC-coated graphite electrodes of longitudal reactors [31].

2.52 Film composition

The Si-N system produced by glow discharge forms a complete range of compositions that is from amorphous silicon containing only a trace amounts of N, to subsilicon nitrides containing an excess of nitrogen compared to stoichiometric compound Si_3N_4. Film stoichiometry is controlled primarily by the ratio of source gas flows, which may be very different from the film stoichiometry. Plasma power and

frequency, and substrate temperature are secondary variables for determining stoichiometry [1].

Most glow discharge silicon nitride films are relatively insoluble except in hydroflouric (HF) or hot phosphoric acids, thus direct chemical determination of composition is difficult [32]. The early and present investigation of the chemical composition of plasma-deposited Si:N:H alloys focussed on the Si/N (or N/Si) concentration ratio, the hydrogen concentration and the ratio of the concentration of Si-H/N-H bonds. These bonds are supposed to determine the physical properties of the plama nitrides [43-45]. It has been established that H content can influnce the physical, chemical and mechanical properties of N-rich films but there is no clear evidence as yet that the H content can influence optical and electrical properties, but it is established that film stoichiometry has the most influence on these properties [13]. The determination of elemental concentrations, hydrogen-related bands concentrations and the presence of impurities such as oxygen and carbon are accessible experimentally, for instance by Rutherford backscattering (RBS) [46], Auger Electron Spectroscopy (AES) [32] and Fourier Transform Infrared (FTIR) spectroscopy. The approximate bulk composition of silicon nitride films is 45 at.% silicon, 34 at.% nitrogen and 21 at.% hydrogen [13].

The Si/N ratio in the film depends on the total gas flow rate, pressure and power and has been found to vary from 0.73-1.20 [42]. The films are generally considered to be Si-rich for Si/N ratio greater than 0.75 and N-rich for Si/N ratio smaller than 0.75 [13]. Si-rich films are formed much more readily probably because Si-H or Si-Si bonds are more easily formed than the sp^2 hybrid orbital of N atoms in planar trigonal arrangement [45]. Generally films closer to stoichiometric composition

(N/Si = 1.33) are obtained as power, temperature and NH_3/SiH_4 ratio are increased while pressure is reduced [31]. Variations in these parameters are caused by differences in dissociation energies for silane and ammonia or nitrogen [11]. While relative chemical bonds of H with Si and N, the Si-H/N-H ratio, depends on temperature, power and silane to ammonia (or nitrogen) flow rate ratio [11,31]. Increasing the silane flow can lead to changes in the distribution of hydrogen favouring increases in Si-H bonds, at the expense of N-H bonds [47].

In the ammonia/silane process, the N/Si concentration ratio was found to follow a square-root dependance on the NH_3/SiH_4 gas-phase ratio [48]. Claassen et al applied mixtures of SiH_4, NH_3 and N_2 in a parallel-plate hot-wall plasma reactor, found that the N/Si ratio is decreased with increasing deposition temperature and increasing total pressure. A drop of the N/Si ratio occurs at a rf of about 4 MHz. It must be noted, however, that these dependancies have been obtained by keeping the growth constant via adjustment of the rf power [45]. It has been found otherwise that the N/Si concentration ratio increases with decreasing plasma power [40].

The H content has been found to lie around 25 at.% and is mainly determined by the substrate temperature, but other values are also reported in the range of 2-40 at.%. There is an appreciable decrease in H content with increasing substrate temperature that is almost exponential [13] and also that the H concentration depends on the gas composition for a given substrate temperature [17,18,49]. In N-rich films most of the H are bonded to N, whereas in N-poor films most of the incorporated H is found in Si-H configurations. Intense efforts have been made to minimize the H content since the incorporated H causes instability in semiconductor devices. One attempt was to replace Si-H bond with Si-F bond, since the Si-F bond has higher

energy. Fujita et al [50-52] attempted to minimize the H content of the Si-N film using SiF_2. It is obtained from reduction of SiF_4 by Si instead of SiH_4. Livenhood and Hess [53] have reported on fluorinated Si-N film deposition using a $SiH_4/He/NH_3/N_2$ system. However most films containing F hydrolyze on exposure to air and hence an understanding of the deposition condition to obtain stable Si-N-F film is still not clear [11].

Upon any increase in N concentration in the plasma nitrides, the IR Si-H (s) mode absorption frequency also increases. This effect is ascribed to the increasing summed electronegativity of the nearest neighbours to the Si atom in which the H atom is bonded, as the N concentration increases [54,55]. In this way IR absorption spectroscopy is a probe for investigating local bonding modes and the nearest-neighbour environment of the H-containing groups [38]. From IR spectroscopy, Maeda and Nakamura [56] indentified three different configurations for Si-H bonding (Si-H groups, $=Si=H_2$ and/or $(=Si-H_2)_n$ chains and $-Si-H_3$ configuratons), and two for N-H bonding (=N-H and $N=H_2$). Of these bonds, $=Si=H_2$ bonds are reported to be the most thermally stable, while the $-N=H_2$ groups were deduced to be more thermally stable than =N-H bonds [56]. Since $N=H_2$ groups are not favourable as regards to chemical stability of the nitride [57], the deposition conditions should be selected so as to minimize the concentration of this network-terminating group. This can be achieved by depositing films with N/Si less than 1.9 [57].

2.53 Optical properties

Optical properties in the region of the absorption edge for glow discharge silicon nitrides of varying composition were reported by Philip [58] and variation in the optical gap in films prepared from silane and ammonia have also been reported [59]. The optical energy gap is commonly deduced from Tauc's plot in the strong absorption region. Typical values obtained for silicon nitrides is around 5.1 eV [60], but however the optical gap can vary from 5 eV for 5% silane concentration in ammonia, to 2.5 eV for a 20% concentration and this corresponds to compositional changes from approximately stoichiometric Si_3N_4 to $SiN_{0.45}$ [58,61]. Similar results investigated by other workers show that the optical gap increases with x where x=N/Si [55,62]. Several workers [63-65] have also reported that the optical energy gap opens at around $x \approx 1.2$ for the SiN_x system. In order to achieve $x \geq 1.2$ it is necessary to use NH_3 in the deposition process, and the use of N_2 on the other hand, to lower the H content shall result in sufficient N incorporation only at high power densities, but however the growth rate is rather low (0.05-0.2 nm/s). The incorporation of H in the SiN_x matrix has a contribution in widening the optical gap particularly on the Si-rich side, which has been reported experimentally by Davis et al [66] and supported by a theoretical caculation utilizing Tight-Binding Model [67]. Also as the deposition temperature increases, the optical gap shifts towards lower energy [13].

Refractive index (n) is among the more commonly film properties measured in order to determine the film quality and establish reproducibility of process control [11]. Refractive index is very much a function of stoichiometry and hence also determined by deposition parameters [11]. The value of the n decreases fairly linearly

from 2.0 for pure nitride to 1.46 for pure oxide [13] where low refractive indices are caused by oxygen impurities [2]. Films that are free of oxygen but have Si/N ratios greater than 0.75 are Si-rich silicon nitride and have a refractive index that increases as the amount of excess Si increased [2]. Thus the gradual changes in composition with change in reactant gas ratio is reflected in the refractive index of the films. Increasing the SiH_4/NH_3 ratio in the gas mixture shall increases the Si/N ratio in the films and this corresponds to an increase in the refractive index [13].High values in n are observed in Si-rich films and it correlates somewhat with Si/N or Si-H/N-H ratio in the film, at least at a constant H concentration and constant deposition temperature, for all samples prepared in one and the same reactor [9,11]. For a H concentration of about 22 at.%, the plasma-deposited material is considered as a nitride when it has a a value for n below 1.97 [45], which corresponds to Si/N values smaller than 0.85. For lower H contents, the values for n are larger for the same Si/N concentration [40]. The refractive index also affected by film density as polarizability per unit volume is related to density by the Lorentz-Lorentz relationship. Hence values of n increases with increasing temperature [68,69]. A plasma silicon nitride layer deposited at 300°C has a value of n of about 1.9 for an Si/N ratio of 0.75, compared with 2.0 for a higher temperature with the same Si/N ratio [45,70]. This difference is due to the large amount of H incorporation in the film's layers [13]. Generally the refractive index is quite unaffected by the chamber pressure or total gas flow rate [72].

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